Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

XII.

On some of the Relations of Salts of Zinc and Alumina to Soda and Potassa.

BY E. N. HORSFORD.

(*Communicated September* 11, 1860.)

ON the addition of caustic soda to a solution of neutral sulphate of zinc there follows a precipitate which disappears in an excess of the soda. A solution of neutral sulphate of alumina exhibits under like conditions the same phenomena, and both salts comport themselves with potassa as they do with soda. Alumina is thrown down from its solutions in potassa and soda by chloride of ammonium and by mineral acids, while oxide of zinc is not in like manner precipitated from its solution in these alkalies.

The following results present some of the quantitative relations of these agents to each other.

Experiments with Sulphate of Zinc.

Strength of Solutions.

1	cubic centimetre of the	solution of sulphate of zinc contains	0.0257	gram. oxide of zinc,
		equal to	0.05108	gram. anhydrous sulphate of zinc.
1	" "	soda solution contains	0.04313	gram. soda.
1	" "	potassa solution contains	0.0230	gram. potassa.

Experiments with Soda.

	ZnO . SO_3.	Required to complete Precipitation. NaO.	Required to precipitate and re-dissolve. NaO.
	5 c. c.	2.3 c. c.	7.6 c. c.
	"	"	"
	"	"	"
	"	"	"
	"	"	"
	"	"	"
Average,	5 c. c.	2.3 c. c.	7.6 c. c.

5 c. c. of solution of	$ZnO . SO_3$	contain	0.1285	gram.	ZnO.
2.3 " "	NaO	"	0.0983	gram.	NaO.

By deducting from 7.6 c. c. the amount 2.3 c. c. required for precipitation, we have the amount required for resolution.

5.3 c. c. of solution of NaO contain 0.2286 gram. NaO.

Now 0.0983 gram. NaO will neutralize 0.1268 gram. SO_3; for

$$31 : 40 = 0.0983 : 0.1268.$$

But the sulphuric acid in 5 c. c. of sulphate of zinc is 0.1269 gram.; for

$$80.5 : 40 : 5 \times 0.05108 = 0.2554 : 0.1269.$$

There is, therefore, required to precipitate oxide of zinc precisely one atom of soda to one atom of sulphate of zinc.

Theory requires of the sulphuric acid to be neutralized . . .	= 49.67	per cent.
Experiment gives for the equivalent of sulphuric acid to the soda employed	49.61	"

The reaction is

$$ZnO . SO_3 + NaO = ZnO + NaO . SO_3.$$

In order to re-dissolve the oxide of zinc 0.2286 gram. of NaO is required, a quantity 2.3 times as great as was required to precipitate it. To ascertain the influence of the quantity of water on the reaction, experiments were made with soda solution, of which 1 c. c. contained 0.1889 gram. of soda.

10 c. c. of the sulphate of zinc solution required, to precipitate and re-dissolve, 2.9 c. c. of soda solution. This is equal to 2.78 equivalents, of which one being employed to precipitate, there remain for resolution 1.78 equivalents. It is obvious, therefore, that the solution of the oxide of zinc is influenced by the quantity of water present. The larger the proportion of water — within the limits of these experiments — the less perfect was the solution of the precipitated oxide.

Experiments with Potassa.

5 c. c. of sulphate of zinc solution required to complete precipitation, as the result of many coincident determinations, 5.1 c. c. of the potassa solution.

5 c. c. of solution of	$ZnO . SO_3$	contain	0.1285	gram.	ZnO
		and	0.1269	"	SO_3.
5.1 " "	KO	contain	0.1173	"	KO.

Now 0.1269 gram. of sulphuric acid requires for neutralization 0.1491 gram. of

potassa, — a quantity to which 0.1173 gram. sustains the relation of 3 : 3.81, or nearly of 3 : 4. It is obvious, therefore, that the chief part of the precipitate was the well-known compound $4\,ZnO\,.\,SO_3$.

Resolution was attended with much greater difficulty. The results were so variable, that no confidence could be placed in them. The influence of water was observed here as in the experiments with soda. The potassa was too dilute.

A more concentrated solution, of which 1 c. c. contained 0.2590 gram. of potassa, gave the following result.

10 c. c. of solution of $ZnO\,.\,SO_3$ required 4 c. c. of solution of KO to precipitate and re-dissolve. Allowing, according to the preceding determination, .75 of an equivalent for the precipitation, there are required to re-dissolve 2.65 equivalents.

Bonnet dissolved two parts of hydrated oxide of zinc in five parts of potassa solution of 1.3 specific gravity. Such a solution contains about .25 part of KO. 5 c. c. would contain 1.25 grammes, which would give about two atoms of zinc dissolving in $1\frac{1}{4}$ of potassa; or the soluble compound would be $8\,ZnO\,.\,5\,KO$. The compound is probably that obtained by Fremy,* — two atoms of oxide of zinc to one of potassa. This compound, upon the slightest addition of water, resolved itself, according to Fremy, into anhydrous oxide of zinc and hydrated potassa. These facts sufficiently explain the difficulty of obtaining satisfactory results in the attempts to re-dissolve with a solution of the strength here employed.

Experiments with Sulphate of Alumina.

Common potassa alum, refined by repeated crystallizations, was dissolved in distilled water.

1 c.c.	of the	alum	solution	contained	0.0371	gram. of	crystallized potassa alum.
"	"	"	"	"	0.009386	"	SO_3, combined with alumina.
"	"	soda	"	"	0.0430	"	NaO.
"	"	potassa	"	"	0.0230	"	KO.
"	"	sulphuric acid	"	"	0.03264	"	SO_3.
"	"	chloride of ammonium	"	"	0.03305	"	NH_4Cl.

Experiments with Soda.

	Alum.	C. c. of Soda required to precipitate.	C. c. of Soda required to precipitate and re-dissolve.	C. c. of Sulphuric Acid required to re-precipitate.	C. c. of Chloride of Ammonium required to re-precipitate.
	10 c. c.	1.4	2.7	1.0	2.9
	"	1.4	2.7	1.0	2.9
	20 c. c.	2.8	5.4	2.0	5.8
	"	2.8	5.4	2.0	5.8
Average,	10 c. c.	1.4	2.7	1.0	2.9

---

* Compt. Rend., XV. p. 1106.

10 c. c. alum solution contain	0.3710	gram.	alum.
" " " "	0.09386	"	SO_3, combined with alumina.
1.4 c. c. soda solution "	0.0602	"	NaO.
" " will neutralize	0.07767	"	SO_3.
2.7 c. c. soda will contain	0.1161	"	NaO.
" " correspond with	0.1498	"	SO_3.

0.09386 gram. SO_3	= 25.30 per cent;	3 atoms	= 25.30 per cent.
0.07767 " "	= 20.93 "	$2\frac{1}{2}$ "	= 21.07 "
0.1498 " "	= 40.37 "	5 "	= 42.15 "

According to these results, two and a half atoms are required completely to precipitate the alumina, and a little more than an equal quantity to re-dissolve the precipitate. Expressing these relations in formulæ we have, omitting the sulphate of potassa of the alum,

$$2\,[Al_2O_3 . 3\,SO_3] + 5\,NaO = \underline{2\,Al_2O_3 . SO_3} + 5\,[NaO . SO_3].$$

$$\underline{2\,Al_2O_3 . SO_3} + 5\,NaO = 2\,[Al_2O_3 . 2\,NaO] + NaO . SO_3.$$

The sulphuric acid of the precipitate may be more or less withdrawn by long continued washing, showing how feeble the affinity is, where the action of water in quantity is brought to bear on both the constituents of the precipitate.

The constitution of the soda and alumina compound in the resolution differs from that of the soluble compound prepared by fusing together alumina and carbonate of soda, by Schaffgotsch,* which had only one atom of soda to one of alumina.

If these two atoms of soda to each atom of alumina require, in order to the precipitation of the alumina, two atoms of sulphuric acid, we have,

$\frac{2}{5}$ of 0.1161 gram. NaO = 0.04644 gram.
0.4644 " NaO correspond with 0.059991 " of SO_3.
1 c. c. of the sulphuric acid solution contained 0.03264 "

a quantity but little more than one half that required to neutralize the SO_3. The formula will be therefore

$$Al_2O_3 . 2\,NaO + SO_3 = \underline{Al_2O_3 . NaO} + NaO . SO_3.$$

It is not to be denied that this result seems inconsistent with the solubility of the compound obtained by Schaffgotsch, unless it be admitted that the alumina which has been combined by heat with soda is modified in its properties.

The precipitation with chloride of ammonium required a little more than a full equivalent. $\frac{2}{5}$ of 0.1161 gram. NaO = 0.4644 gram., and require 0.8014 gram.

---

* Pogg. Ann., LIII. p. 117.

NH_4Cl. Experiment gave 0.9580 gram. NH_4Cl, a ratio of 5 : 6. These relations may be expressed by the formula

$$5\,(Al_2O_3 . 2\,NaO) + 12\,NH_4Cl = 5\,\underline{(Al_2O_3 . 2\,NH_3)} + 10\,NaCl + 2\,NH_4Cl.$$

The occurrence of the surplus NH_4Cl suggested the following experiment. With a given alum solution in soda as above, three solutions of sal-ammoniac were taken, of relative strengths as 1 : 2 : 3.

10 c. c. of the soda solution of alumina required of No. 1 for complete precipitation 0.3 c. c.
" " " " " " No. 2 " " 1.0 "
" " " " " " No. 3 " " 2.5 "

If we multiply the number of cubic centimetres of the strongest by three, and that of the medium by two, we have 0.9 : 2 : 2.5, showing that the more concentrated is much more efficient proportionally than is due to the excess of chloride of ammonium it contains. In other words, that in proportion as the quantity of water is increased, so is the efficiency of the reagents enfeebled.

Experiments with Potassa.

	Alum.	Potassa required to precipitate.	Potassa required to precipitate and re-dissolve.	Sulph. Acid required to re-precipitate.	Chloride of Ammonia required to re-precipitate.
	10 c. c.	3.2 c. c.	7.3 c. c.	1.5 c. c.	4.3 c. c.
	"	"	"	"	"
	"	"	"	"	"
Average,	10 c. c.	3.2 c. c.	7.3 c. c.	1.5 c. c.	4.3 c. c.

10 c. c. of the alum solution contain	0.3710	gram.	alum.
" " " "	0.09386	"	SO_3, combined with alumina.
3.2 c. c. of the potassa solution contain	0.07360	"	KO.
7.3 " " " "	0.16790	"	KO.
3.2 " " " will neutralize	0.06263	"	SO_3.
7.3 " " " "	0.1429	"	SO_3.

0.09386 gram. SO_3	= 25.30	per cent ;	3	atoms	= 25.30 per cent.
0.06263 " "	= 16.88	"	2	"	= 16.86 "
0.14290 " "	= 38.52	"	$4\frac{1}{2}$	"	= 37.95 "

According to these results, two atoms are required to precipitate, and a little more than two and a half to re-dissolve. Expressing these relations in formulæ, we have,

$$Al_2O_3 . 3\,SO_3 + 2\,KO = \underline{Al_2O_3 . SO_3} + 2\,[KO . SO_3].$$

$$2\,\underline{[Al_2O_3 . SO_3]} + 5\,KO = 2\,Al_2O_3 . 3\,KO + 2\,[KO . SO_3].$$

The precipitate is the same as that which, according to Berzelius, is thrown down by ammonia, and identical in the relations of alumina to sulphuric acid with native *aluminite.* The compound formed in the resolution differs from the compound obtained by Unverdorben,* and in crystallized form by Fremy,† by saturating boiling potassa with alumina, in that it contains half an atom of potassa more. This is not more striking than the contrast displayed between the compound in the resolution of alumina in soda, and the body produced by Schaffgotsch by melting carbonate of soda and alumina together.

The sulphuric acid required to re-precipitate the alumina somewhat exceeded one equivalent.

1½ atoms KO = ¾ of 0.0736 gram. = 0.0552 gram. KO.
0.0552 gram. KO correspond with 0.0469 " SO_3.
1.5 c. c. of sulphuric acid solution contain 0.04896 " SO_3.

The formula most nearly expressing the reaction would be,

$$2\,Al_2O_3 . 3\,KO + 3\,SO_3 = \underline{2\,Al_2O_3} + 3\,[KO . SO_3].$$

It appears, therefore, that while all the alumina is thrown down by sulphuric acid from its soda solution with an equivalent of soda in combination not saturated, it is not entirely precipitated from its potassa solution by the same reagent till all the potassa has been withdrawn by the sulphuric acid, or till an equivalent of sulphuric acid for all the potassa has been added.

The chloride of ammonium required to re-precipitate the alumina from its solution in potassa is somewhat more than two equivalents of the chloride to one of the potassa in combination with the alumina.

1½ atoms of KO = 0.0552 gram., which corresponds with 0.0626 gram. NH_4Cl.
4.3 c. c. of chloride of ammonium solution contain 0.1421 " NH_4Cl.

It is doubtless true with this, as with the corresponding soda result, that the quantity of chloride of ammonium required to produce precipitation, is influenced by the degree of dilution of the reagents.

The above result is most nearly expressed by the formula,

$$2\,[Al_2O_3 . 3\,KO] + 6\,NH_4Cl = 2\,\underline{[Al_2O_3 . 3\,NH_3}] + 6\,KCl.$$

The compound most nearly allied to this is Rose's compound of chloride of aluminum and ammonia,

$$Al_2Cl_3, 3\,NH_3,$$

obtained by passing dry ammoniacal gas over chloride of aluminum. ‡

---

* Pogg. Ann., VII. p. 323.

† Compt. Rend., XV. p. 1106.

‡ Pogg. Ann., XXIV. p. 228.

The foregoing results may be presented in the following formulæ.

Sulphate of Zinc and Soda.

1. $ZnO . SO_3 + NaO = \underline{ZnO} + NaO . SO_3.$

Sulphate of Zinc and Potassa.

2. $4 [ZnO . SO_3] + 3 KO = \underline{4 ZnO . SO_3} + 3 [KO . SO_3].$

Sulphate of Alumina and Soda to Precipitation and Resolution.

3. $2 [Al_2 O_3 . 3 SO_3] + 5 NaO = \underline{2 Al_2 O_3 . SO_3} + 5 [NaO . SO_3].$
4. $\underline{2 Al_2 O_3 . SO_3} + 5 NaO = 2 [Al_2 O_3 . 2 NaO] + NaO . SO_3.$

Re-precipitated with Sulphuric Acid.

5. $Al_2 O_3 . 2 NaO + SO_3 = \underline{Al_2 O_3 . NaO} + NaO . SO_3.$

Re-precipitated with Chloride of Ammonium.

6. $5 [Al_2 O_3 . 2 NaO] + 12 NH_4 Cl = 5 \underline{[Al_2 O_3 . 2 NH_3]} + 10 NaCl + 2 NH_4 Cl,$

or, probably,

$$Al_2 O_3 . 2 NaO + 2 NH_4 Cl = \underline{Al_2 O_3 . 2 NH_3} + 2 NaCl.$$

Sulphate of Alumina and Potassa to Precipitation and Resolution.

7. $Al_2 O_3 . 3 SO_3 + 2 KO = \underline{Al_2 O_3 . SO_3} + 2 [KO . SO_5].$
8. $2 \underline{[Al_2 O_3 . SO_3]} + 5 KO = 2 Al_2 O_3 . 3 KO + 2 [KO . SO_3].$

Re-precipitated with Sulphuric Acid.

9. $2 Al_2 O_3 . 3 KO + 3 SO_3 = \underline{2 Al_2 O_3} + 3 [KO . SO_3].$

Re-precipitated with Chloride of Ammonium.

10. $2 Al_2 O_3 . 3 KO + 6 NH_4 Cl = 2 [Al_2 O_3 . 3 NH_3] + 6 K Cl.$

It is probable that in some of these reactions the salts, represented in the formulæ as in solution, are in part more or less firmly combined with the precipitates. It is unquestionable that water enters into the constitution of many of the precipitates. The formulæ give only the relations of the quantities to the facts of precipitation, resolution, and re-precipitation. They illustrate, also, incidentally, the influence of water on the efficiency of a reagent.